1/1 DWPI - (C) Thomson Derwent
AN - 1987-040176 [06]
XA - C1987-016979
TI - Aq. concentrated dye soln. used in paper and dyeing industries - comprises brown dye and water-soluble poly-alkylene glycol
DC - A23 A60 E21 F06
PA - (NIKC) NIPPON KAGAKU KOGYOSHO KK
NP - 2
NC - 1
PN - JP61296069 A 19861226 DW1987-06 4p *
AP: 1985JP-0136871 19850625
- JP95000748 B2 19950111 DW1995-06 C09B-067/26 3p
FD: Based on JP61296069
AP: 1985JP-0136871 19850625
PR - 1985JP-0136871 19850625
AB - **JP61296069 A**
Aq. concentrated dye soln. comprises brown dye (A) and water-soluble polyalkylene glycol. X is Li, -NH2(CH2CH2OH)2, -NH(CH2CH2OH)3, n is 1 or 2.
- Pref. (A) is obtd. by coupling of a diazonium salt obtd. from C.I. Basic Brown 1 and 1-aminonaphthalene-3-sulphonic acid, with the pH adjuster of LiOH, Li2CO3, di- or tri-ethanolamine. Salt has more solubility in water than the known salt (Na or K). Polyalkylene glycol is polyethylene- or polypropylene-glycol. (Deg. of polymsn., above 3 Mol.wt., below 20000).
- USE/ADVANTAGE - Used for paper and dyeing industries (cellulose, silk, wool, polyamide fibre, leather, etc.). Prod. improved the stability with high concn. (10-40%) and eliminated working efficiency and environment problems. (0/0)

(19) Japanese Patent Office (JP)

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(54) Title of the invention: Aqueous concentrated dye solution composition

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(22) Application date: 25th June 1985

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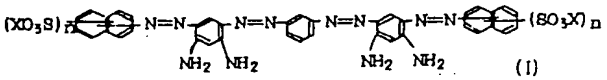
Specification

1. Title of the invention

Aqueous concentrated dye solution composition

2. Scope of the patent claim

A stable aqueous concentrated solution composition, characterised in that it contains a brown dye represented by the general formula

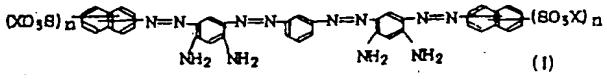


(I)

(in the formula, X independently represents Li, $-NH_2(CH_2CH_2OH)_2$ or $-NH(CH_2CH_2OH)_3$, and n represents the number 1 or 2) and a water-soluble polyalkylene glycol.

3. Detailed description of the invention

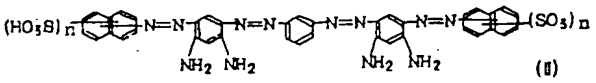
The present invention relates to a novel stable concentrated aqueous solution composition for a brown tetrakisazo dye represented by the general formula



(I)

(in the formula, X independently represents Li, $-NH_2(C_2H_4OH)_2$ or $-NH(CH_2CH_2OH)_3$, and n represents the number 1 or 2).

Conventional brown tetrakisazo dyes of general formula



(II)

(in the formula, n is as defined above) are commercially available and are used in practice in the form of finely ground powders of the sodium salt, in some cases obtained by compounding with suitable diluting agents and auxiliary agents; it is well known, however, that such powder dyes have many disadvantages in terms of the operating environment, operational efficiency, quality control of the dyed products, and so forth. There is strong demand from the dye industry and the paper production industry, the consumers, for the provision of a concentrated, stable aqueous solution composition.

When, in response to these demands, aqueous solutions of the sodium salt of the dye have been obtained, it has only been possible to obtain solutions of low concentration, around 2% at 25°C, and these change over time, with the precipitation of insolubles and discoloration occurring readily, and no counter-measures have been discovered.

The main aim of the present invention is therefore the provision of a high concentration, stable brown dye aqueous solution composition with which the above-mentioned disadvantages are completely overcome.

The present inventors' research resulted in the discovery that when the acid groups of a brown tetrakisazo dye are converted into lithium salts, diethanolamine salts or triethanolamine salts, as in above-mentioned general

formula (I), the hydrophilicity and ease of solvation are greatly increased, for example to approximately 20% (lithium salt), or to approximately 40% (diethanolamine salt), at 25°C; and it also resulted in the discovery that the stability is specifically improved by the addition of water-soluble polyalkylene glycol at from 1 to 40% with respect to the weight of the whole composition (dye + water + polyalkylene glycol).

By means of the present invention it is possible to obtain a highly concentrated, very stable aqueous solution composition of brown tetrakisazo dye containing from about 10 to 40%, with respect of the weight of the whole composition, of pure dye component, which is ideal and completely different from the prior art.

The brown tetrakisazo dye used as the dye component in the inventive novel concentrated aqueous solution can itself be prepared according to well-known methods.

For example, most usefully, the tetrakisazo dye represented by general formula (I) can be prepared in the form of a lithium, diethanolamine or triethanolamine salt, or a mixture thereof, by subjecting C.I. Basic Brown 1 and a naphthylamine monosulphonic acid such as 1-aminonaphthalene-3, -4, or -5-sulphonic acid or 2-aminonaphthalene-1-, -3-, -5-, -6-, -7- or -8-sulphonic acid, and a naphthylamine disulphonic acid such as 1-aminonaphthalene-4,6-, -4,7- or -5,7-disulphonic acid or 2-aminonaphthalene-3,6-, -3,7-, -4,7-, -5,7-, -4,8- or -6,8-disulphonic acid, to diazo conversion by a known method, then coupling the resulting diazonium salts at a

molar ratio of approximately 1:2 using lithium hydroxide, lithium carbonate, diethanolamine or triethanolamine while adjusting the pH.

The above-mentioned tetrakisazo dye can also be obtained by dissolving the corresponding sodium salt in water, precipitating the acid using hydrochloric acid or sulphuric acid, obtaining the precipitating free acid by filtration then adding lithium hydroxide, lithium carbonate, diethanolamine or triethanolamine to the resulting free acid wet cake. Salts obtained in this way are novel and do not appear in the literature, and have much better water-solubility than known sodium salts and potassium salts.

The present invention is an aqueous solution composition comprising brown tetrakisazo dye, which is a novel salt as described above, and polyalkylene glycol. The polyalkylene glycol used in the present invention may be added after the aqueous solution of tetrakisazo dye has been prepared, or it can be prepared as an aqueous solution beforehand, and then the tetrakisazo dye can be dissolved in this. It is also possible to add the polyalkylene glycol to the reaction solution during the process of producing the brown tetrakisazo dye in the form of a novel salt as described above, for example, during the coupling reaction. Obviously, in such cases the resulting mixture may be diluted or concentrated as appropriate to obtain the dye at the specified final concentration.

Polyethylene glycol, polypropylene glycol and the like can be used as the water-soluble polyalkylene glycol in the

present invention. Such polyalkylene glycols having a degree of polymerization of at least 3, and a molecular weight of no greater than approximately 2000 are preferred. Interestingly, dialkylene glycols such as diethylene glycol are not expected to afford the advantages of the present invention. The amount of these [polyalkylene glycols] used should be, usually, from 1 to 40%, particularly preferably from 3 to 10% by weight with respect to the weight of the concentrated aqueous solution as the final target substance, and by using such an amount it is possible to obtain a highly stable, highly concentrated aqueous solution composition.

The inventive dye aqueous solution composition may, if necessary, also contain various additives known to those skilled in the art, and examples include glycols such as ethylene glycol and diethylene glycol, polyhydric alcohols such as glycerin, alcohols such as isopropyl alcohol, water-soluble organic solvents such as dioxane, dimethyl sulfoxide, formamide, dimethylacetamide, dimethyl-formamide, tetrahydrofuran and glycol monoalkyl ethers, acid amide compounds such as urea, alkylurea and ε-caprolactam, aliphatic amines such as triethylamine, propanolamine and ethyldiethanol amine, and various surfactants and defoaming agents. These supplementary additives can be selected by those skilled in the art according to the intended final use of the aqueous dye solution.

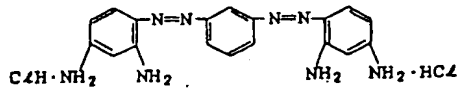
Brown trisazo dye concentrated aqueous solution of the present invention can be used not only to dye various types of natural and recycled cellulose, and cellulose

derivatives such as acetyl cellulose, examples of which include paper and wood pulp, but also for the dying brown of natural and synthetic polyamide materials such as silk, wool, polyamide fibres and leather. Specifically, the present invention is particularly useful for dying polyamide materials such as those mentioned above when the brown tetrakisazo dye is in the form of a lithium tetrasulphonate.

The present invention is described more specifically below by means of working examples. In said description, "parts" refers to "parts by weight".

Working example 1

Diazo formation was performed by a common method, in that 49.0 parts of sodium naphthionate were dissolved in 400 parts of water, 57.4 parts of 35% hydrochloric acid were added, then a solution obtained by dissolving 140 parts of sodium sulphite in 40 parts of water was added at 20°C. The naphthionic acid diazonium salt which precipitated on completion of the diazo formation was obtained by filtration, and 80 parts of the resulting wet cake were mixed with 41.9 parts of C.I. Basic Brown 1 obtained by a common method and having a structure represented by the formula



100 parts of water, 20.0 parts of polyethylene glycol (mw 400) and 20.0 parts of urea to form a uniform slurry,

coupling was performed using triethanolamine at 10°C while adjusting the pH to 8, and on completion of said coupling, the system was heated to 30°C and made up to a total of 300 parts using water, then the small insoluble component was removed to yield a concentrated solution composition. This composition contained 27% dye component in the form of free acid, it could be diluted to any degree using cold water, and no changes whatsoever were seen after storage for 6 months. Conversely, a sodium salt dye of the prior art was such that only 2% dissolved in water at 25°C and only 5% dissolved in water at 80°C.

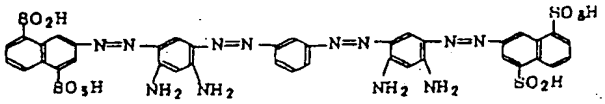
The above-mentioned composition was diluted using water, and the resulting solution was used as a stock solution for the continuous dying of pulp to obtain brown paper products. The dye uniformity of the resulting products was extremely good.

Use example 1

Continuous dying was performed as follows: 0.1 part of the dye solution composition obtained in Working example 1 was introduced into 330 parts of pulp solution of L.B.K.P 30 g/l, degree of beating 25 SR, the system was agitated thoroughly for 10 minutes, then 0.1 part of sizing agent was introduced, and after a further 10 minutes, 0.3 parts of anhydrous aluminium sulphate were added, and the system was agitated for 10 minutes. When this was used to make paper, brown paper of excellent dye uniformity was obtained.

Working example 2

Wet cake containing 90 parts of dye having a structure represented by formula



was obtained by acid precipitation of a sodium salt dye obtained by common means, and a mixture comprising 200 parts of said wet cake, 17.5 parts of lithium hydroxide monohydrate, 15 parts of polypropylene glycol (mw 200) and 39 parts of water was heated to 40°C to obtain a uniform brown solution, then the small amount of insoluble residue was removed to yield a concentrated solution composition. This composition contained 36% by weight of dye in the form of free acid.

An experiment was conducted in the same way as in Working example 1, with the result that this composition could be diluted to any degree using cold water, and no changes whatsoever were seen after storage for 6 months. It should be noted that a high concentration, high stability composition was also obtained as described above when diethanolamine was used in an amount equimolar to the above-mentioned lithium hydroxide.

Use example 2

Chrome-tanned leather was washed using water for 60 minutes, drawn at a wringing rate of 100% using a mangle roller, then 20 parts thereof were treated in a drum for 5 minutes using 100 parts of water and 0.4 parts of sodium

bicarbonate, then, after washing using water for 20 minutes, 100 parts of water and 0.2 parts of the dye solution composition obtained in Working example 2 were added, dying was allowed to proceed for 30 minutes at from 40 to 50°C, then 0.6 parts of greasing agent were added and greasing treatment was performed for 30 minutes at from 45 to 50°C.

Next, the remaining water in the dyeing drum was discarded, 100 parts of fresh water and 0.2 parts of 90% formic acid were added, and treatment was allowed to proceed for 10 minutes at 40°C, whereupon the product was washed using water and dried to yield chrome-tanned leather that had been dyed brown with excellent dye uniformity.

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Translator's note
Japanese proper nouns can have several possible readings; common readings have been chosen throughout.

⑲日本国特許庁(JP)　⑪特許出願公開

⑫公開特許公報(A)　昭61-296069

⑤1Int.Cl.⁴	識別記号	庁内整理番号	㊸公開 昭和61年(1986)12月26日
C 09 B 67/24		7433-4H	

審査請求 未請求 発明の数 1 (全4頁)

㊹発明の名称　水性濃厚染料溶液組成物

㉑特　願　昭60-136871
㉒出　願　昭60(1985)6月25日

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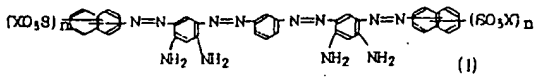
明　細　書

1. 発明の名称　水性濃厚染料溶液組成物

2. 特許請求の範囲

一般式

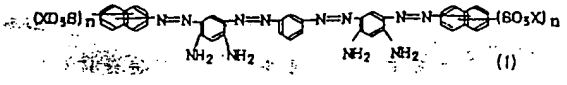


(I)

(式中Xはそれぞれ独立にLi、$-NH_2(CH_2CH_2OH)_2$または$-NH(CH_2CH_2OH)_3$であり、そしてnは1または2の数を示す)で表わされる、褐色染料と水溶性ポリアルキレングリコールを含有することを特徴とする、安定な水性濃厚溶液組成物。

3. 発明の詳細な説明

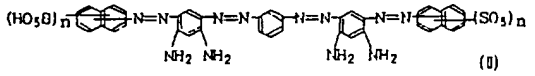
本発明は一般式



(I)

(式中Xはそれぞれ独立にLi、$-NH_2(C_2H_4OH)_2$または$-NH(CH_2CH_2OH)_3$であり、そしてnは1または2の数を示す)で表わされる、褐色テトラキスアゾ染料の新規な安定濃厚な水性溶液組成物に関する。

従来一般式



(II)

(式中nは前記と同じ意味を表わす)の褐色色テトラキスアゾ染料はナトリウム塩の微細に粉砕された粉末の形、そして場合によつては適当な希釈剤および助剤を配合した形で市販され且つ実用化されているが、これら粉末染料は作業環境、作業能率および染色物の品質管理上等多くの欠点を有することは良く知られている。需要先である製紙業界や染色業界から濃厚且つ安定な水性溶液組成物の提供を強く要望されている。

このような要望に対して本染料はそのナトリ

ウム塩の形で水溶液にした場合低濃度、２５℃で２％程度のものが得られるにすぎずしかもそれは経時的変化、不溶解物の析出および変色を起しやすく、その解決策が見出されていなかつた。

したがつて本発明の主たる目的は前述したような欠点を完全に克服した高濃度、かつ安定な褐色染料水溶液組成物を提供するのにある。

本発明者等の研究によれば前記一般式(I)の褐色テトラキスアゾ染料を形成する酸基をリチウム塩ジエタノールアミン塩またはトリエタノールアミン塩にすることにより、例えば２５℃において２０％（Li塩）ないし約４０％（ジエタノールアミン塩）程度に親水性および易溶性が増大することを見出し、さらに水溶性ポリアルキレングリコールを全組成物（染料＋水＋ポリアルキレングリコール）重量あたり１～４０％添

加することにより安定性が特異的に向上することを見出した。

本発明によれば従来と全く異なつた理想的な純染料分全組成物重量あたり１０～４０％を含む高濃度できわめて安定な褐色テトラキスアゾ染料の水性溶液組成物を得ることができる。

本発明の新規な濃厚水性溶液中で染料成分として使用される褐色テトラキスアゾ染料は、それ自体既知の方法を使用して製造することができる。

例えばもつとも有利にはC.I. Basic Brown 1とナフチルアミンモノスルホン酸類例えば１－アミノナフタリン－３、－４、または－５－スルホン酸、２－アミノナフタリン－１－、－３－、－５－、－６－、－７－、または－８－スルホン酸およびナフチルアミンジスルホン酸類例えば１－アミノナフタリン－４,６－または－４,７－また

は－５,７－ジスルホン酸、２－アミノナフタリン－３,６－、－３,７－、－４,７－、－５,７－、－４,８－、および－６,８－ジスルホン酸を公知の方法でジアゾ化した、ジアゾニウム塩を約１：２のモル比で水酸化リチウム、炭酸リチウム、ジエタノールアミンまたはトリエタノールアミンでpHを調整しつつカップリングさせ一般式(I)で表わされるテトラキスアゾ染料のリチウム、ジエタノールアミンまたはトリエタノールアミン塩およびそれらの混合物を製造しうる。

あるいはまた上述したテトラキスアゾ染料は相当するナトリウム塩を水に溶解させ塩酸または硫酸で酸析し、析出する遊離酸を沪過して次いで得られた遊離酸の湿ケーキに水酸化リチウム、炭酸リチウム、ジエタノールアミンまたはトリエタノールアミンを加えることによつても得られる。このようにして得られた塩は文献未

載の新規な塩であつて、既知のナトリウム塩またはカリウム塩に比して顕著に増大した水溶性を示す。

本発明は上述のような新規な塩である褐色テトラキスアゾ染料と共に、ポリアルキレングリコールを含有せしめてなる水性溶液組成物である。本発明においてはポリアルキレングリコールはテトラキスアゾ染料の水溶液を調製した後で添加してもよいし、あるいはまたこれらを先に水溶液とした後でこれにテトラキスアゾ染料を溶解させてもよい。あるいはまた前述したような新規な塩としての褐色テトラキスアゾ染料生成過程で例えばカップリング反応過程でその反応溶液にポリアルキレングリコールを添加することもできる。もちろんこの場合には得られた添加混合物を所定の最終染料濃度となるように適宜希釈または濃縮して差支えない。

本発明において使用する水溶性ポリアルキレングリコールとしてはポリエチレングリコール、ポリプロピレングリコール等があげられる。これらポリアルキレングリコールは重合度3以上であつて分子量約2000以下のものが好ましい。ジエチレングリコールのようなジアルキレングリコールでは本発明の効果を期待しえないことは興味深いことである。これらは通常最終目的物としての濃厚水溶液重量の1～40%特に好ましくは3～10重量%の量で使用されるのがよく、そのようにすることによつて高安定高濃度な水性溶液組成物を得ることが可能である。

本発明にかかる染料水溶液組成物は、なお必要に応じて当業者には既知の種々の添加剤を含有させることができ、例えばエチレングリコール、ジエチレングリコールのグリコール類、グリセリンのごとき多価アルコール、イソプロピ

ルアルコール等のアルコール類、ジオキサン、ジメチルスルホオキシド、ホルムアミド、ジメチルアセトアミド、ジメチルホルムアミド、テトラヒドロフラン、グリコールモノアルキルエーテル類等の水溶性有機溶剤、尿素、アルキル尿素、ε-カプロラクタム等の酸アミド化合物類、トリエチルアミン、プロパノールアミン、エチルジエタノールアミン等の脂肪族アミン類および各種界面活性剤、消泡剤等があげられる。このような補足的添加剤は染料水溶液の最終用途に応じて当業者により適宜選択されるものである。

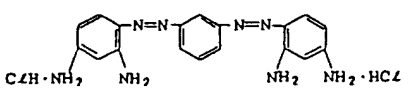
本発明による褐色トリスアゾ染料濃厚水溶液は種々の天然または再生セルロースまたはアセチルセルロースのごときセルロース誘導体、例えば紙、木綿等の染色のみならず絹、羊毛、ポリアミド繊維、皮革などの天然または合成ポリ

アミド材料を褐色に染色するのに使用できる。特に本発明において褐色テトラキスアゾ染料がテトラスルホン酸リチウム型の場合には上述したようなポリアミド材料の染色に対して特に有用である。

以下実施例により具体的に本発明を説明する。説明中「部」とあるのは「重量部」を示す。

実施例　1

ナフチオン酸ソーダ49.0部を水400部に溶解し35%塩酸57.4部を加えた後、20℃で亜硝酸ソーダ14.0部、水40部に溶解した液を加え公知の方法でジアゾ化する。ジアゾ化終了後析出したナフチオン酸のジアゾニウム塩を戸別することにより得られた湿ケーキ80部を公知の方法で得られた、式



の構造を有するC.I. Basic Brown 1 41.9部、水100部、ポリエチレングリコール(MW400) 20.0部、尿素20.0部と伴に均一なスラリーとし10℃においてトリエタノールアミンでpH 8に調整しながらカップリングを終了させ、次いで30℃に昇温し水で全仮を300部とした後わずかな不溶解分を除去すれば濃厚な液状組成物が得られた。この組成物は遊離酸の形の染料分27%を含有しており、冷水で任意の割合で希釈することができ6ケ月間保存しても何等の変質も認められなかつた。これに対して従来のナトリウム塩の染料は水に対して25℃に於て2%、80℃に於て5%溶解するにすぎない。

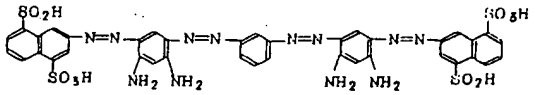
上記の組成物を水で希釈しこれをストック液としてパルプを連続的に染色すると褐色の紙製品を得る。この得られた染色物の均染性は極めて良好である。

使用例　1

叩解度25SRのL.D.K.P.30g/lのパルプ溶液330部の中へ実施例1で得られた染料溶液組成物0.1部を入れ10分間よく撹拌した後サイズ剤0.1部を入れ、更に10分後無水硫酸アルミニウム0.3部を添加し、10分間撹拌を続けて染色する。これを抄紙すると褐色の均染性の優れた紙を得る。

実施例　2

公知の方式で得られた、ナトリウム塩の染料を酸析することにより得られた式



の構造をもつた染料90部を含む湿ケーキ200部、水酸化リチウム1水塩17.5部、ポリプロピレングリコール（MW200）15部、水39部の混合物を40℃に加温して均一な褐色溶液と

し少量の不溶解残渣を除去すると濃厚な溶液組成物が得られた。この組成物は遊離酸の形の染料36重量%を含有する。

実施例1と同様な試験を行つた結果、この組成物は冷水で任意の割合に希釈することができ、6ケ月間保存しても何等の変質も認められなかつた。なお別に前記で水酸化リチウムと等モルのジエタノールアミンを使用しても同様に前記のごとく高濃度且つ高安定な組成物が得られた。

使用例　2

クロム鞣甲皮を60分間水洗しマングルローラで絞り率100%とした後、それの20部をドラム中で水100部および重炭酸ナトリウム0.4部で5分間処理し、20分間水洗した後水100部および実施例2で得られた染料溶液組成物0.2部を加えて40～50℃で30分間染色後、さらに加脂剤0.6部を加えて45～50℃で30分間

加脂処理を行つた。

その後染色ドラムの廃水を捨て、新たに水100部および90%蟻酸0.2部を加えて40℃で10分間処理した後に水洗乾燥すると均染性のすぐれたクロム鞣甲皮の褐色染色物を得る。

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外2名